

Synthesis, Crystal Structure and Fluorescent Property of d-f Heterodinuclear Eu(III)-M(II) (M=Cd(II), Ni(II)) Cryptates.

Qiu Yun CHEN^{1*}, Qin Hua LUO², Zhi Lin WANG², Jiu Tong CHEN³

¹Department of Chemistry, Huangshan College, Huangshan 245021

²Coordination Chemistry Institute, Nanjing University, Nanjing 210093

³Fuzhou State key Laboratory of Structure Chemistry, Fuzhou 350002

Abstract: This communication reports the reports the synthesis, crystal structure and the fluorescent property of cryptates [EuML(DMF)](ClO₄)₂ (M=Cd, Ni).

Keywords: Heterodinuclear cryptates, europium(III), fluorescent property.

The design of ligands capable of forming stable and strong luminescent Eu³⁺ complexes is a theme of great interest. Because such complexes have potential use as luminescent molecular label for biological study¹ and luminescent materials for lasers². The cryptates have good thermodynamic stability and kinetic inertness toward metal dissociation. The pioneer studies on lanthanide polyaza-cryptates containing three 2, 2'-bipyridines and their N-oxides have been presented by J. M. Lehn, and coworker³. Since 1995 iminophenolate (Robson - type) cryptates have been aroused great interest³⁻⁴. The first homodinuclear lanthanide cryptates was obtained in 1999⁵. Very recently, a 'Robson-type' Dy(III)-Cu(II) heterodinuclear cryptate was reported by us⁶. The synthesis and photophysical properties of heterodinuclear cryptates containing both transition metal ions and europium(III) ions have not been reported. Herein, we report the synthesis, crystal structure and fluorescent property of the cryptates [EuML(DMF)](ClO₄)₂ (M=Cd(II), Ni(III), L denotes deprotonated anionic cryptand synthesized by condensation of tris(2-aminoethyl)amine (tren) with 2,6-diformyl -4-chloro-phenol (dcp)).

Preparation

The mononuclear europium(III) cryptate ([Eu(H₃L)(NO₃)(H₂O)](ClO₄)₂, **1**)⁷ (0.120 g, 0.1 mmol) was dissolved in methanol(15 mL) with small amount of DMF(1.0 mL). The above solution was stirred with solid CaH₂ for 2 hour, the pH of the solution changed from 6 to 7-8. M(ClO₄)₂ (M=Cd, Ni) (0.1 mmol) was added and the reaction mixture was refluxed for *ca.* 4 h. The solution was concentrated until formation of the

*E-mail: chenqiu_yun@hotmail.com

precipitate **2** or **3**.

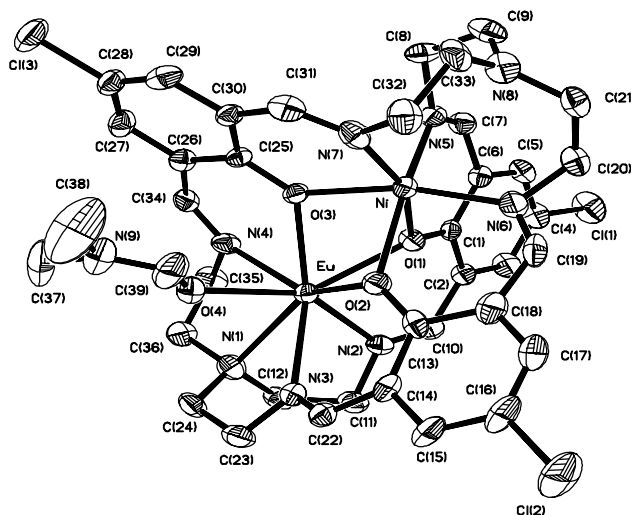
[EuCdL(DMF)](ClO₄)₂ (**2**) Yield: 60%. Anal. for C₃₉H₄₃Cl₅N₉O₁₂CdEu: Calcd. C, 36.84; H, 3.41; N, 9.91, Cd, 8.84; Eu, 11.95. Found: C, 36.72; H, 3.54; N, 9.80; Cd, 8.76; Eu, 11.98%. IR (KBr, cm⁻¹): 1643s [ν(C=N)]; 1541s [ν(C-O)]; 1089s [ν(ClO₄-)]; 625m [ν(ClO₄-)]. Λ_m (DMF, 298k) 142 S·cm²·mol⁻¹.

[EuNiL(DMF)](ClO₄)₂·MeCN (**3**) Yield, 45%. Anal. for C₄₁H₄₆Cl₅N₁₀O₁₂EuNi: Calcd. C, 39.12; H, 3.91; N, 11.12; Found: C, 39.45; H, 3.98; N, 10.78%. IR (cm⁻¹): 1645s [ν(C=N)]; 1541s [ν(C-O)]; 1089s [ν(ClO₄-)]; 625m[ν(ClO₄-)]. Λ_m (DMF, 298k) 145 S·cm²·mol⁻¹. The crystal suitable for X-ray diffraction was obtained by recrystallization from the acetonitrile-methanol solution.

X-ray Crystallography

A yellow crystal with dimensions of 0.36 × 0.18 × 0.10 mm was used for X-ray diffraction. The unit cell parameters and the diffracted intensities were measured at room temperature using a graphite-monochromated Mo-κ α ($\lambda = 0.71073$ Å) radiation. ω -2 θ scan mode was employed. Total of 20201 reflections were collected in the range of $1.05 \leq \theta \leq 25.01^\circ$, of which 8659 were unique. The structure was solved by direct method. All H-atomic coordinates were calculated theoretically and fixed during refinement.

Figure 1 The crystal structure of [EuNiL(DMF)]²⁺



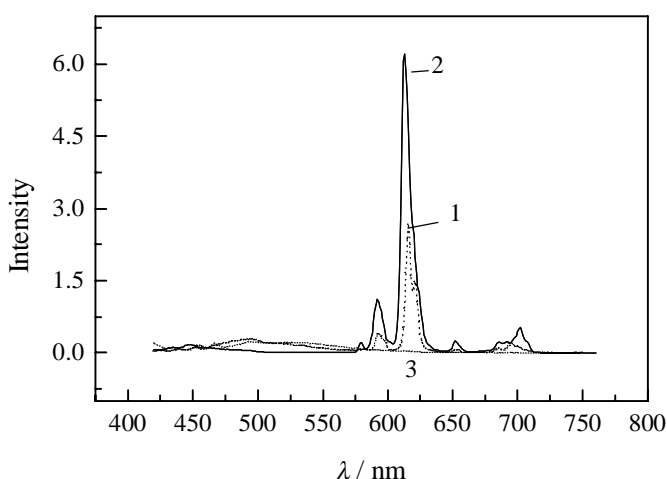
The existence of Eu(III)-Ni(II) heterodinuclear cryptate is confirmed by the single-crystal determination. Crystallographic data: C₄₁H₄₆Cl₅N₁₀O₁₂EuNi, Mr = 1258.80, monoclinic, space group P2₁/c, a=19.6676(5), b=11.8492(3), c=21.5154(6) Å, $\beta=98.0300(10)^\circ$, Z=4, V=4964.9(12), D_c=1.684 g/cm³, F₀₀₀=2536, R=0.0716, R_w=0.1452. The crystal structure of [EuNiL(DMF)]²⁺ is shown in **Figure 1**. The Eu³⁺ and Ni²⁺ are encapsulated in the cavity and bridged by the oxygen atoms O(1), O(2), O(3)

of deprotonated phenyl groups. The Eu(III) ion is located at one end of the cavity and is eight coordinated by three imino nitrogen atoms N(2), N(3), N(4), three phenolate oxygen atoms and one of the bridgehead nitrogen N(1). The coordination configuration is best described as distorted dodecahedron. The other end of the cavity was occupied by a Ni(II) ion, three μ -phenolate oxygen atoms and three imino nitrogen atoms coordinated to the Ni(II), forming a distorted octahedral configuration. The distance between Eu(III) and Ni(II) ions is 3.220 Å. Further detailed studies on this cryptate will be reported shortly.

Fluorescent Properties of Cryptates (1)-(3)

Emission of cryptates (1)-(3) in MeCN solution with light at 400 nm were shown in **Figure 2**. Compared with the mononuclear europium(III) cryptate **1**, there is no obvious emission band in the range 420-750 nm for cryptate **3**, indicating the fluorescence of Eu(III) ion in the cavity was completely quenched by the encapsulated Ni(II) ion. However, the characteristic emission spectrum of Eu(III) ion for cryptate **2** was observed. All emissions arise from the 5D_0 level corresponding to the $^5D_0 \rightarrow ^7F_j$ ($\Delta J=0, 1-4$) transition. The weak band at 580 nm arises from the $^5D_0 \rightarrow ^7F_0$ transition. The band around 593 nm for $^5D_0 \rightarrow ^7F_1$, which is magnetic-dipole allowed, is hardly affected by a change of the coordination environment. The intense band around 613 nm for $^5D_0 \rightarrow ^7F_2$ is an electric-dipole allowed transition and its emission intensity is sensitive to the coordination environment of Eu(III)⁸. The ratios of the intensities of the $^5D_0 \rightarrow ^7F_2$ to the $^5D_0 \rightarrow ^7F_1$ transition for cryptate **1** and **2** are 7.8 and 6.2 respectively. The luminescent quantum yield for cryptate **2** was 1.8 times higher than that of cryptate **1**. These shows that fluorescence emission of Eu(III) ions in the cryptates was influenced by the encapsulated transition metal ions.

Figure 2 The emission spectra for the cryptates.



Note: The mononuclear $[\text{Eu}(\text{H}_3\text{L})(\text{NO}_3)(\text{H}_2\text{O})](\text{ClO}_4)_2$ (**1**) and heterodinuclear cryptates $[\text{EuML}(\text{DMF})](\text{ClO}_4)_2$ (M=Cd, (**2**); Ni (**3**)) in MeCN solution at an excitation wavelength of 400nm.

Acknowledgments

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